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(54) **POWDER COATING COMPOSITIONS AND A METHOD FOR COATING A SUBSTRATE**

**PULVERBESCHICHTUNGSZUSAMMENSETZUNGEN SOWIE VERFAHREN ZUR
STUBSTRATBESCHICHTUNG**

**COMPOSITIONS DE REVETEMENT EN POUDRE ET PROCEDE DE REVETEMENT D'UN
SUBSTRAT**

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**EP-A- 0 410 242 FR-A- 2 091 106
GB-A- 1 443 715 US-A- 4 078 015**

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Description

This invention is concerned with improvements relating to powder coating compositions and methods of coating substrates using such compositions.

Powder coating is a well-established process, basically comprising the application of a powdered fusible material to a substrate, heating of the powder in contact with the substrate to cause the powder to melt and re-flow, and cooling the resultant melt to form a solid coating on the substrate. The coating material may simply comprise a film-forming thermoplastic material or may comprise a reactive material, e.g. an epoxy resin together with a curing agent therefore, so that during the course of melting and reflowing reaction occurs to cure the material in situ on the substrate. In any event, powder coating materials are generally such that they have to be melted and reflowed at relatively high temperatures, e.g. 150°C or more. As a result, powder coating processes are generally not suitable for the coating of heat-sensitive materials such as wood or plastics material. In order to coat such materials, it would be necessary to have a product which had a relatively low melting temperature, e.g. below 120°C, whilst at the same time being solid at ambient temperature, which material could subsequently be cured in situ on the substrate during the melting/reflowing stage or, afterwards.

U.S. -A-4 093 674 discloses a thermosetting powder coating composition comprising a solid resin having a T_g from 5° to 150°C and free hydroxyl groups and a solid polyisocyanate compound, with a molar ratio of isocyanate groups in the latter to active hydrogen in the former of 0.2 to 2. Among examples of the solid resin are the polymers of hydroxyalkylacrylates preferably with Mn from 1 000 to 30 000. This powder coating composition is said to provide advantages over isocyanate crosslinking-type urethane resins wherein all the isocyanate groups are previously blocked with a phenol or an alcohol.

G.B. -A-1 590 413 discloses a urethane resin having at least 2 terminal ethylenically unsaturated groups and comprising the reaction product of at least one isocyanate-functional prepolymer and at least one unsaturated monomer having a single isocyanate-reactive-hydrogen-containing group, said isocyanate-functional prepolymer being the reaction product of (i) at least one diisocyanate and (ii) a mixture of at least 2 polyols (at least 30 mole % being polymeric and at most 70 mole % being monomeric in the said mixture) in an NCO : OH ratio of at least 2.3. This urethane resin is mixed with similar unsaturated materials derived from polymeric polyols, with the unreacted excess of diisocyanate and with a reactive diluent which at the end produces flowable and fluid compositions with viscosities of 4.5 Pa.s. No mention of powder coating may be found in this document.

U.S. -A-4 500 696 discloses powder surface coatings comprising polyols and a polyisocyanate compo-

nent comprising blocked adducts of aliphatic diisocyanates. They involve no unsaturated alcohol.

U.S. -A-5 089 586 discloses acrylate-free water-dispersible allyl urethanes prepared from a polyglycol or its reaction product with an unsaturated dicarboxylic acid, a hydroxyallyl compound (preferably an allyl ether) and a diisocyanate.

International Application WO-93/19132 discloses mixtures, in a binder composition for powder coatings, of an unsaturated polyester and an oligomer having a plurality of allyl ether groups and having further urethane groups.

EP-A-0 410 242 relates to a powder coating composition which comprises the reaction product of one or more organic polyisocyanates with one or more monovalent alcohols containing (meth)acryloyl groups, and one or more compounds which are free from (meth)acryloyl groups and contain at least two isocyanate-reactive groups.

FR-A-2 091 106 relates to a process for preparing a polymer having C=C double bonds, capable of being polymerized, comprising a polyisocyanate which allows to bind an ester which contains polymerizable C=C double bonds and which has active H, to a matter containing several H.

GB-1 443 715 refers to a copolymerizable fluid composition comprising a photocopolymerizable ethylenically unsaturated liquid monomer, a photosensitizer and a photopolymerizable divinylurethane monomer prepared from xylylene diisocyanate, (meth)acrylic esters having a hydroxyl group and di-, tri-, tetra-, penta- or hexavalent alcohol.

US-A-4 078 015 concerns a copolymerizable composition including a polymerizable acrylic diurethane and a polymerizable polyacrylic polyurethane which is the reaction product of an organic diisocyanate, a β-hydroxy alkyl ester of an acrylic acid, and a diol.

It has now been found, in accordance with the present invention, that useful solid ethylenically unsaturated materials, having relatively low melting point and suitable for use in powder coating compositions may be prepared by reacting a diisocyanate with one or more monohydric alcohols, optionally in combination with a monomeric polyol such as a dihydric alcohol.

According to one embodiment of the invention, therefore, there is provided a powder coating composition comprising a powdered solid ethylenically unsaturated material having a melting point from 60° to 120°C obtained by reacting a polyisocyanate with an at least stoichiometric amount of an alcoholic component comprising :

- at least one monohydric alcohol with an ethylenic unsaturation derived from acrylic acid or methacrylic acid and at least one monohydric alcohol free from ethylenic unsaturation derived from acrylic acid or methacrylic acid, and optionally
- at least a monomeric polyol.

Said monomeric polyol can be a dihydric aliphatic alcohol or a dihydric polyalkylene glycol.

In accordance with a preferred embodiment of the invention the polyisocyanate is reacted with an at least stoichiometric amount of :

- (i) a monohydric alcohol component, or
- (ii) a monohydric alcohol component followed by another different monohydric alcohol component, or
- (iii) a monohydric alcohol component, followed by a dihydric alcohol component, followed by a monohydric alcohol component, or
- (iv) a dihydric alcohol component, followed by a monohydric alcohol component alone or in admixture with a dihydric alcohol component,

the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol, at least a part of which bearing an ethylenic unsaturation derived from acrylic acid or methacrylic acid and the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being preferably used in an amount not more than 50%, preferably not more than 25%, of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the polyisocyanate.

As noted above, it is a requirement of the present invention that the material obtained (hereinafter simply referred to as an "oligourethane", "urethane acrylate" or "oligomer") have a melting point of from 60 to 120°C (the term "melting point" as used herein means the melting point as determined by the ring and ball method).

It is also most often preferred that the powdered solid material of the invention have a viscosity in the range from 0.1 Pa.s to 2.5 Pa.s.

Suitable polyisocyanates for use in the preparation of the oligourethanes include toluene diisocyanate, diphenylmethane-4,4'-diisocyanate, hexamethylene-1,6-diisocyanate, naphthylene-1,5-diisocyanate, 3,3'-dimethoxy-4,4'-biphenyldiisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate, phenylene diisocyanate, 4,4'-biphenyldiisocyanate, isophorone diisocyanate, trimethylhexamethylene diisocyanate and tetramethylene xylene diisocyanate.

A wide variety of monohydric aliphatic alcohols may be used to produce the oligourethanes, e.g. C₁ to C₂₂ alcohols. Typical etherified dihydric alcoholic materials which may be used as monohydric alcoholic component include propylene glycol methyl ether, dipropylene glycol methyl ether, ethylene glycol butyl ether, diethylene glycol butyl ether, tripropylene glycol butyl ether and propylene glycol phenyl ether. Dihydric alcohols which may be used include, for example, saturated aliphatic diols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, butylene glycols, neopentyl glycol, 1,3- and 1,4-butane diols, 1,5-pentane diol, 1,6-hexanediol,

2-methyl-1,3 propanediol, glycerol, and 1,1,1-trimethylolpropane.

The reaction between the polyisocyanate and the monohydric/dihydric alcohol component is suitably carried out in the presence of a catalyst. As such a catalyst the following may be mentioned :

- (a) tertiary amines such as bis(dimethyl amino ethyl)ether, trimethyl amine, triethyl amine, N-methyl morpholine, N-ethyl morpholine, N,N-dimethyl benzylamine, N,N-dimethyl ethanol amine, N,N,N',N'-tetramethyl-1,3-butane diamine, triethylanol amine, 1,4-diazabicyclo(2.2.2.)octane and pyridine oxide,
- (b) tertiary phosphines such as trialkyl phosphines and dialkyl benzyl phosphines,
- (c) strong bases such as the hydroxides, alcoholates and phenolates of alkali metals and alkaline earth metals,
- (d) metal salts of strong acids such as ferric chloride, stannic chloride and bismuth chloride, antimony trichloride and bismuth nitrate,
- (e) chelates, such as those which can be obtained from acetyl acetone, benzoyl acetone, trifluoroacetyl acetone, ethyl acetoacetate, salicylaldehyde, cyclopentanone-2-carboxylate, acetyl acetoinimine, bis-acetyl acetone alkylene diimines, salicylaldehyde imine, and from metals such as beryllium, magnesium, zinc, cadmium, lead, titanium, zirconium, tin, arsenic, bismuth, chromium, molybdenum, manganese, iron, cobalt and nickel,
- (f) alcoholates and phenolates of metals, such as Ti(OR)₄, Sn(OR)₄, Sn(OR)₂ and Al(OR)₃, in which R is an alkyl or aryl group,
- (g) the metal salts of organic acids, such as alkali metals and alkaline earth metals, aluminium, tin, lead, manganese, cobalt, nickel and copper, for example sodium acetate, potassium laurate, calcium hexanoate, stannous acetate, stannous octoate and stannous oleate, lead octoate, manganese and cobalt naphthenates, and
- (h) iron and cobalt metal carbonyls and organometallic derivatives of tetravalent tin, of trivalent and pentavalent arsenic, of antimony and of bismuth ; particularly preferred are the salts of dialkyl tin carboxylic acids, such as dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin maleate, dilauryl tin diacetate, dioctyl tin diacetate, dibutyl tin bis(4-methylamino benzoate), dibutyl tin bis(6-methylamino caproate), trialkyl tin hydroxides, dialkyl tin oxides, dialkyl tin dialkoxides and dialkyl tin dichlorides.

Said catalyst is generally used at a rate of from 0.01 to 2% by weight of the polyisocyanate.

The molecular weight of the final solid, ethylenically unsaturated material is suitably from 500 to 3 000, preferably from 500 to 1 500.

For some applications it is desirable that the oli-

gourethanes be clear. It is not possible to predict whether any particular oligourethane produced in accordance with the invention will, or will not, have the desired optical properties in this respect. However, here again it is a matter of simple routine trial and experiment.

The ethylenically unsaturated solid material forming a part of the powder coating composition in accordance with the invention is in powdered form, e.g. has an average particle size from 10 to 250 μm , especially from 10 to 90 μm . In addition to the particulate, ethylenically unsaturated material, a powder coating composition in accordance with the invention preferably further comprises a curing system for the ethylenically unsaturated material.

In accordance with one embodiment of the invention, the curing system may comprise a thermally initiated free radical-generating catalyst, of the peroxide type or, optionally together with one or more promoters therefore. Suitable examples of such free radical-generating catalysts include 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane, 1,1-bis (t-butylperoxy)-cyclohexane, t-butylperoxy-isopropyl carbonate, t-butyl perisononanoate, t-butyl peracetate, t-butyl perbenzoate, dicumyl peroxide, di-t-butyl peroxide, t-butyl hydroperoxide, t-butyl perneodecanoate, diisooctanoyl peroxide, dibenzoyl peroxide, and azo bis (isobutyronitrile).

Preferably, the catalyst system is selected so that the powder can melt and reflow prior to curing. This makes it possible to obtain a level film, in contrast to conventional epoxy/acid powders in which curing is effected during melting and reflowing, leading to an orange peel effect.

In accordance with another embodiment of the invention, the curing system may further comprise one or more photoinitiators, sensitive to ultraviolet light, optionally together with sensitizers therefore. By operating with such a system, the coating composition may be allowed to cool and solidify after melting/reflowing and then be subjected to appropriate irradiation to cure the coating.

Examples of suitable photoinitiators include benzoyldimethyl ketal, trimethylbenzophenone, isopropylthioxanthone, ethyl 4-dimethylamino benzoate, benzophenone, 2-chloro and 2-ethyl-thioxanthone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenyl-propanone, 4-benzoyl-4'-methyl-diphenyl sulphide, 1-hydroxycyclohexyl-acetophenone, and 2-ethyl-hydroquinone.

Examples of suitable sensitizers include 4,4-dimethylamino-benzophenone, triethanolamine, N-methyldiethanolamine, 2-(butoxy)ethyl, 4-dimethylamino benzoate and acrylated amines.

In accordance with another embodiment of the invention, the curing system may be absent and curing of the solidified coating on the substrate may be effected by electron beam.

In addition to the basic components noted above,

powder coating compositions in accordance with the invention may, and often do, contain at least one other ingredient particularly selected from colorants such as pigments or dyestuffs, flow aids, anti-cissing agents, flexibilizers, degassing agents and inorganic fillers.

The invention also provides a powder coating process for coating a substrate which comprises applying a powder coating composition in accordance with the invention to the substrate, heating the composition to melt and reflow it on the substrate, and allowing the composition to cool on the substrate. In the case of the first embodiment of the invention discussed above, curing of the coating will preferably be effected by free radical polymerisation after the melting/reflowing step, whereas in the second embodiment of the invention an additional curing step is required that is the substrate bearing the cured coating must be subjected to ultraviolet or electron beam radiation.

In order that the invention may be well understood the following example is given by way of illustration only. Unless stated otherwise, all amounts are expressed by weight.

EXAMPLE

250 g of diphenyl methane-4,4'-diisocyanate and 0.1 g of dibutyl tin dilaurate were charged to a 1 litre round bottomed flask fitted with a thermometer, air sparge and an addition funnel. The contents were heated to 45°C and 37 g of dipropylene glycol methylether were added and the temperature allowed to rise to 60°C. Then 67.5 g of octadecanol was charged and the temperature raised to 110°C, at which temperature 0.5 g of hydroquinone was added. An air sparge was set at 1.5 l/hour and bubbled through the material while 116 g of hydroxyethyl acrylate was added over 1 hour while maintaining the batch temperature at 110°C until the isocyanate value falls below 30 mgKOH/g. Then 33.5 g of dipropylene glycol was charged and the batch temperature raised to 120°C and held until the NCO value is lower than 30 ppm. The urethane acrylate was then discharged and allowed to cool. It was found that the material produced was a very hard solid with a melting point of 101°C and had a extremely low viscosity of only 0.1 Pa.s at 125°C. This material is called Resin B.

Resin B was extruded with 0.5% of a thermal initiator benzoyl peroxide and 2% of Modaflow®, at a screw speed of 200 rpm giving a residence time in the extruder of 10 seconds. The temperature was maintained between 110 and 115°C with the wall temperature between 120 and 125°C. The final product has a gel time of 3.5 minutes at 110°C. The resultant material was then ground and classified to less than 90 μm and electrostatically applied to a chromated aluminium test panel. The panel was then reflowed and cured in a fan assisted oven at 120°C for 10 minutes to yield a film with a Koenig hardness of 80% and a methyl ethyl ketone swab resistance of more than 200 rubs.

Claims

1. A powder coating composition comprising a powdered solid ethylenically unsaturated material having a melting point from 60° to 120°C obtained by reacting a polyisocyanate with an at least stoichiometric amount of an alcoholic component comprising :
 - at least one monohydric alcohol with an ethylenic unsaturation derived from acrylic acid or methacrylic acid and at least one monohydric alcohol free from ethylenic unsaturation derived from acrylic acid or methacrylic acid, and optionally
 - at least a monomeric polyol.
2. A powder coating composition according to claim 1, characterized in that a monohydric alcohol comprises a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol.
3. A powder coating composition according to any of claims 1 and 2, characterized in that the monomeric polyol is a dihydric aliphatic alcohol or a dihydric polyalkylene glycol.
4. A powder coating composition according to claim 3, characterized in that the said dihydric aliphatic alcohol or dihydric polyalkylene glycol is used in an amount not more than 50% of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups of the polyisocyanate.
5. A powder coating composition according to any of claims 1 to 4, characterized in that the powdered solid material has a viscosity in the range from 0.1 Pa.s to 2.5 Pa.s.
6. A powder coating composition according to any of claims 1 to 5, characterized in that the reaction of the polyisocyanate with the alcoholic component is carried out in the presence of a catalyst selected from tertiary amines, tertiary phosphines, strong bases, metal salts of strong acids, chelates, metal alcoholates and metal phenolates, metal salts of organic acids, iron and cobalt carbonyls, and organometallic derivatives of tetravalent tin, of trivalent and pentavalent arsenic, antimony and bismuth.
7. A powder coating composition according to any of claims 1 to 6, characterized in that the molecular weight of the solid ethylenically unsaturated material is from 500 to 3 000.
8. A powder coating composition according to any of claims 1 to 7, characterized in that the solid ethy-

enically unsaturated material has an average particle size from 10 to 250 µm.

9. A powder coating composition according to any of claims 1 to 8, characterized in that it further comprises a curing system for the ethylenically unsaturated material.
10. A powder coating composition according to claim 9, characterized in that the curing system comprises a thermally initiated free-radical generating catalyst.
11. A powder coating composition according to claim 9, characterized in that the curing system comprises a photoinitiator sensitive to ultraviolet light.
12. A powder coating composition according to claim 11, characterized in that the curing system further comprises a sensitizer.
13. A powder coating composition according to any of claims 1 to 12, characterized in that it further comprises at least one other ingredient selected from pigments or dyestuffs, flow aids and inorganic fillers.
14. A method of coating a substrate which comprises applying a coating composition according to any of claims 1 to 13 to the substrate, heating the composition to melt and reflow it on the substrate, and allowing the composition to cool on the substrate.

Patentansprüche

1. Pulverlackzusammensetzung, enthaltend ein pulverförmiges, festes, ethylenisch ungesättigtes Material mit einem Schmelzpunkt von 60 bis 120°C, das erhältlich ist durch Umsetzung eines Polyisocyanats mit einer zumindest stöchiometrischen Menge einer Alkoholkomponente, enthaltend:
 - mindestens einen von Acrylsäure oder Methacrylsäure abgeleiteten, ethylenisch ungesättigten einwertigen Alkohol und mindestens einen von Acrylsäure oder Methacrylsäure abgeleiteten, nicht ethylenisch ungesättigten einwertigen Alkohol und gegebenenfalls
 - mindestens ein monomeres Polyol.
2. Pulverlackzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß es sich bei einem einwertigen Alkohol um einen einwertigen aliphatischen Alkohol oder einen veretherten oder veresterten zweiwertigen aliphatischen Alkohol oder ein verethertes oder verestertes zweiwertiges Polyalkylenglykol handelt.

3. Pulverlackzusammensetzung nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, daß es sich bei dem monomeren Polyol um einen zweiwertigen aliphatischen Alkohol oder um ein zweiwertiges Polyalkylenglykol handelt.
4. Pulverlackzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß der zweiwertige aliphatische Alkohol oder das zweiwertige Polyalkylenglykol in einer Menge von höchstens 50% der zur Reaktion mit den Isocyanatgruppen des Polyisocyanats erforderlichen stöchiometrischen Menge von Hydroxylgruppen verwendet wird.
5. Pulverlackzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das pulverförmige, feste Material eine Viskosität im Bereich von 0,1 Pa.s bis 2,5 Pa.s aufweist.
6. Pulverlackzusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Umsetzung des Polyisocyanats mit der Alkoholkomponente in Gegenwart eines Katalysators aus der Gruppe bestehend aus tertiären Aminen, tertiären Phosphanen, starken Basen, Metallsalzen starker Säuren, Chelaten, Metallalkoholaten und Metallphenolaten, Metallsalzen organischer Säuren, Eisen- und Cobaltcarbonylen sowie metallorganischen Derivaten des vierwertigen Zinns und des drei- oder fünfwertigen Arsens, Antimons oder Bismuts durchgeführt wird.
7. Pulverlackzusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das feste, ethylenisch ungesättigte Material ein Molekulargewicht von 500 bis 3000 aufweist.
8. Pulverlackzusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß das feste, ethylenisch ungesättigte Material eine durchschnittliche Teilchengröße von 10 bis 250 µm aufweist.
9. Pulverlackzusammensetzung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß sie außerdem auch noch ein Härtungssystem für das ethylenisch ungesättigte Material enthält.
10. Pulverlackzusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß das Härtungssystem einen thermisch initiierten radikalbildenden Katalysator enthält.
11. Pulverlackzusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß das Härtungssystem einen gegenüber ultraviolettem Licht empfindlichen Photoinitiator enthält.

12. Pulverlackzusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das Härtungssystem außerdem auch noch einen Sensibilisator enthält.

13. Pulverlackzusammensetzung nach einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß sie außerdem auch noch mindestens einen anderen Bestandteil aus der Gruppe bestehend aus Pigmenten oder Farbstoffen, Rieselhilfen und anorganischen Füllstoffen enthält.

14. Verfahren zum Beschichten eines Substrats, bei dem man eine Lackzusammensetzung nach einem der Ansprüche 1 bis 13 auf ein Substrat aufbringt, die Zusammensetzung durch Erhitzen auf dem Substrat aufschmilzt und wieder zum Fließen bringt und die Zusammensetzung auf dem Substrat abkühlen läßt.

Revendications

1. Composition de revêtement en poudre comprenant un matériau solide pulvérulent éthyléniquement insaturé, ayant un point de fusion allant de 60° à 120°C, obtenue par réaction d'un polyisocyanate avec une quantité au moins stoechiométrique d'un composant alcoolique comprenant:
 - au moins un alcool monohydrique ayant une insaturation éthylénique dérivée de l'acide acrylique ou de l'acide méthacrylique et au moins un alcool monohydrique dépourvu d'insaturation éthylénique dérivée de l'acide acrylique ou de l'acide méthacrylique, et éventuellement
 - au moins un polyol monomère.
2. Composition de revêtement en poudre selon la revendication 1, caractérisée en ce qu'un alcool monohydrique comprend un alcool aliphatique monohydrique ou un alcool aliphatique dihydrique ou polyalkylèneglycol dihydrique étherifié ou estérifié.
3. Composition de revêtement en poudre selon l'une quelconque des revendications 1 et 2, caractérisée en ce que le polyol monomère est un alcool aliphatique dihydrique ou un polyalkylèneglycol dihydrique.
4. Composition de revêtement en poudre selon la revendication 3, caractérisée en ce que ledit alcool aliphatique dihydrique ou polyalkylèneglycol dihydrique est utilisé en une quantité non supérieure à 50% de la quantité stoechiométrique de groupes hydroxyle nécessaire pour faire réagir les groupes isocyanate du polyisocyanate.
5. Composition de revêtement en poudre selon l'une

quelconque des revendications 1 à 4, caractérisée en ce que le matériau solide pulvérulent possède une viscosité dans la gamme de 0,1 Pa.s à 2,5 Pa.s.

6. Composition de revêtement en poudre selon l'une quelconque des revendications 1 à 5, caractérisée en ce que la réaction du polyisocyanate avec le composant alcoolique est effectuée en présence d'un catalyseur choisi parmi des amines tertiaires, des phosphines tertiaires, des bases fortes, des sels métalliques d'acides forts, des chélates, des alcoolates métalliques et des phénolates métalliques, des sels métalliques d'acides organiques, des fer- et cobalt-carbonyles, et des dérivés organométalliques de l'étain tétravalent, de l'arsenic trivalent et pentavalent, de l'antimoine et du bismuth. 5 10 15
7. Composition de revêtement en poudre selon l'une quelconque des revendications 1 à 6, caractérisée en ce que le poids moléculaire du matériau solide éthyléniquement insaturé est de 500 à 3 000. 20
8. Composition de revêtement en poudre selon l'une quelconque des revendications 1 à 7, caractérisée en ce que le matériau solide éthyléniquement insaturé possède une granulométrie moyenne de 10 à 250 μm . 25
9. Composition de revêtement en poudre selon l'une quelconque des revendications 1 à 8, caractérisée en ce qu'elle comprend en outre un système de durcissement pour le matériau éthyléniquement insaturé. 30
10. Composition de revêtement en poudre selon la revendication 9, caractérisée en ce que le système de durcissement comprend un catalyseur générant des radicaux libres amorcés thermiquement. 35
11. Composition de revêtement en poudre selon la revendication 9, caractérisée en ce que le système de durcissement comprend un photoamorceur sensible à la lumière ultraviolette. 40
12. Composition de revêtement en poudre selon la revendication 11, caractérisée en ce que le système de durcissement comprend en outre un sensibilisateur. 45
13. Composition de revêtement en poudre selon l'une quelconque des revendications 1 à 12, caractérisée en ce qu'elle comprend en outre au moins un autre ingrédient choisi parmi des pigments ou des colorants, des auxiliaires d'écoulement et des charges inorganiques. 50 55
14. Procédé de revêtement d'un substrat qui comprend les étapes consistant à appliquer une composition

de revêtement selon l'une quelconque des revendications 1 à 13 sur le substrat, chauffer la composition pour la faire fondre et la refaire s'écouler sur le substrat, et laisser la composition refroidir sur le substrat.